

A Comparison of Silica and Carbon as Adsorbents When Used in Non- Aqueous Binary Solutions

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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George H. Scheffler

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. F. E. Bartell for his helpful advice in the direction of this investigation.



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I—ADSORPTION BY SILICA FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE

An interferometric method for measurement of adsorption by carbon from binary organic liquid systems was described in earlier papers from this Laboratory.¹ It was shown that, in every case investigated, the curve representing adsorption over the entire concentration range was S-shaped. The component having the higher adhesion tension against carbon was adsorbed to the greater extent. The component of lower adhesion tension was, however, preferentially adsorbed if present in sufficiently low concentration. An equation was derived which was based on the assumption that adsorption of each component of a binary liquid system follows the Freundlich equation. The equation $H \Delta x/m = ax^n(1-x) - b(1-x)^d x$ thus obtained was used to calculate the preferential adsorption over the concentration range.²

It is quite well known that carbon adsorbs better from aqueous solutions than from organic liquids, while silica adsorbs better from organic liquids.³ Carbon has been shown to have a high adhesion tension against non-polar organic liquids and a relatively low adhesion tension against certain polar organic liquids and water;⁴ the converse is true for silica.⁵ From

¹ Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1637 (1929); **51**, 1643 (1929).

² The symbols used in this paper are the same as those of earlier papers

H = total number of millimoles in the solution

x = mole fraction solute at equilibrium

Δx = mole fraction change due to adsorption

m = weight of adsorbent

c_0 = initial concentration

c = final concentration

Δc = change in concentration due to adsorption

N = total weight (in grams) of solution

a, n, d and b are constants

³ Patrick and Jones, *J. Phys. Chem.*, **29**, 1 (1925).

⁴ Bartell and Osterhof, *Ind. Eng. Chem.*, **19**, 1277 (1927).

⁵ Bartell and Miller, *ibid.*, **20**, 738 (1928).

previous investigations in this Laboratory it has been shown that, other factors being equal, adsorption should be greatest from that liquid which has the lowest adhesion tension against a given solid adsorbent. This explains why adsorption by carbon should be greater from an aqueous solution, and why adsorption by silica should be greater from organic liquids. In the present work the interferometric method was used to determine concentration changes which occurred during the process of adsorption. Binary organic liquid systems were used with silica as the adsorbent. The results obtained are compared with those previously obtained with carbon. The experimental procedure employed was that described by Bartell and Sloan.¹

Preparation of Silica.—The silica used was prepared by a method similar to that which had previously been used in this Laboratory.⁶ A sodium silicate solution of 1.02 specific gravity was treated with concentrated hydrochloric acid in the presence of nickel nitrate. The silica gel thus formed was allowed to synerize slowly. The resulting brownish-black material was digested in conductivity water to remove nickel nitrate. This gel was then heated to 260° for two hours and again digested in conductivity water. After the nickel salt had been removed in this manner, the "silica gel" (about 15 g. per batch) was heated at 1000° for four minutes in order further to dehydrate it. At this stage the "silica" was perfectly white. It was next allowed to cool in dry nitrogen and then transferred to flasks also filled with dry nitrogen. A sufficient quantity of the "silica" was prepared to insure that uniform samples might be used throughout the course of the work.

Purification of Liquids.—Standard methods were employed for the purification of the liquids. Each liquid, after preliminary treatment, was distilled through a tall fractionating column with a large area of cooling surface. The middle fractions only were used. The liquid systems investigated were: (1) ethyl carbonate–benzene, (2) ethyl alcohol–benzene, (3) ethyl carbonate–dimethylaniline, and (4) ethyl carbonate–methyl benzoate.

Results

Adsorption from the System Ethyl Carbonate–Benzene.—The adsorption data obtained for this system when plotted give an S-shaped curve. This curve is shown in Fig. 1. Ethyl carbonate was preferentially adsorbed until a concentration of 0.68 mole fraction of it was reached. Beyond this concentration benzene was preferentially adsorbed. The values of the constants were determined by the method used by Bartell and Sloan.¹ The equation representing the adsorption over the entire concentration range for the above system is

$$H\Delta x/m = 7.603 (x)^{0.674} (1 - x) - 8.1798 (1 - x)^{0.982} (x)$$

⁶ Bartell and Fu, "Colloid Symposium Monograph," Vol. VII, 1930.

The agreement between the values calculated from the equation and the values determined experimentally is shown in Table I.

TABLE I
ADSORPTION OF ETHYL CARBONATE FROM BENZENE

c_0	m , g.	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H \Delta x}{m}$ obs.	$\frac{H \Delta x}{m}$ calcd.	Difference
0.0100	0.20	0.00837	0.03587	0.00556	0.31919	0.31725	-0.00194
.0500	.20	.04635	.08054	.02962	.69526	.69026	-.00500
.1000	.20	.09515	.10780	.06274	.94686	.93245	-.01441
.2000	.20	.19478	.11725	.13264	1.07050	1.06020	-.01010
.3000	.20	.29543	.10379	.20954	0.98678	0.98534	-.00144
.7483	.20	.74808	.00555	.66250	.06303	.04617	-.01691
.8883	.20	.88862	-.00804	.84062	-.09750	-.11301	+.01551
.9500	.20	.95031	-.00747	.92359	-.09738	-.09692	-.00046
.9850	.20	.98512	-.00299	.98668	-.03925	-.03930	+.00050

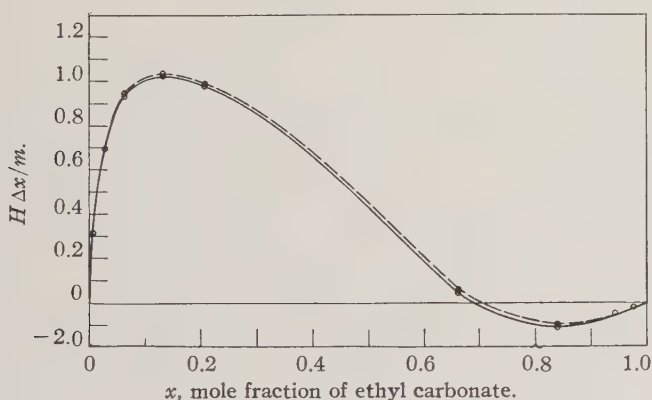


Fig. 1.—Experimental points, — — — —; $7.603 (x)^{0.674} (1 - x) - 8.1798 (1 - x)^{0.982} (x)$, —————, Adsorption of ethyl carbonate from benzene.

Adsorption from the System Ethyl Alcohol-Benzene.—The results obtained with the system ethyl alcohol-benzene give an S-shaped curve, as shown in Fig. 2. Ethyl alcohol in this system is highly adsorbed at a low concentration of this component. Preferential adsorption of benzene is indicated at high alcohol concentrations.

The data obtained for the system alcohol-benzene are given in Table II. The equation representing the adsorption of this system is

$$H \Delta x / m = 8.8105 (x)^{0.227} (1 - x) - 4.664 (1 - x)^{0.615} (x)$$

For purposes of comparison, data obtained with carbon as an adsorbent¹ are plotted also in Fig. 2.

Adsorption from the System Ethyl Carbonate-Dimethylaniline.—In the system ethyl carbonate-dimethylaniline, preferential adsorption of each component is noted over some part of the concentration range.

TABLE II
ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H \Delta x}{m}$
0.01436	0.2622	0.00601	0.1388	0.01014	3.0108
.02745	.2503	.01720	.1783	.02882	3.8299
.04217	.2608	.03001	.1952	.04984	4.1564
.13070	.2534	.12810	.2071	.19928	4.1312
.29195	.2186	.28320	.1656	.40021	3.0001
.74883	.2540	.74810	+ .0112	.83430	0.1596
.90157	.2675	.90288	— .0200	.94035	— .2676
.96640	.2577	.96745	— .0160	.98053	— .2083

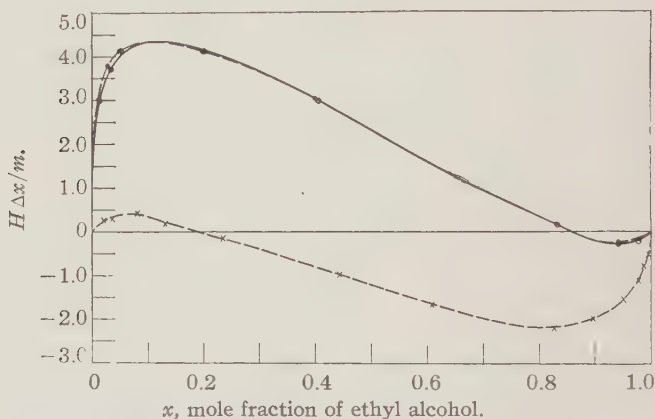


Fig. 2.—Silica (experimental), ———; carbon (experimental), × ———; $8.8105(x)^{0.227}(1-x) - 4.664(1-x)^{0.615}(x)$, O ———. Adsorption of ethyl alcohol from benzene.

Data for this system are given in Table III, and the corresponding adsorption curve in Fig. 3. The equation representing the results obtained is

$$H \Delta x/m = 1.0448 (x)^{0.658} (1 - x) - 0.645 (1 - x)^{0.784} (x)$$

TABLE III
ADSORPTION OF ETHYL CARBONATE FROM DIMETHYLANILINE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H \Delta x}{m}$
0.01194	0.2708	0.01129	0.00835	0.01158	0.07074
.07870	.3230	.07736	.01604	.07923	.13566
.1703	.3802	.16802	.02129	.17168	.17964
.3442	.2983	.34252	.02176	.34838	.18276
.6748	.2930	.67409	.00920	.67975	.07661
.9300	.3125	.93004	.00046	.93171	— .00378
.9894	.2419	.98948	.00119	.98974	— .00985
.9958	.2581	.99585	.00067	.99600	— .00550

Adsorption from the System Ethyl Carbonate-Methyl Benzoate.—
In this system, as in the others, preferential adsorption of each of the two

components occurred over some portion of the concentration range. The adsorption curve for this system is shown in Fig. 4 and the data are given

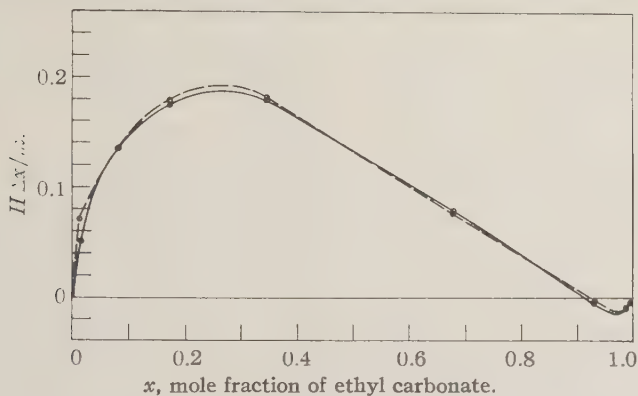


Fig. 3.—Experimental points, — — — — —; $1.0448 (x)^{0.658} (1 - x) - 0.645 (1 - x)^{0.784} (x)$, —————. Adsorption of ethyl carbonate from dimethylaniline.

in Table IV. The adsorption data obtained for this system are represented by the equation

$$H \Delta x / m = 0.8479 (x)^{0.591} (1 - x) - 0.1619 (1 - x)^{0.246} (x)$$

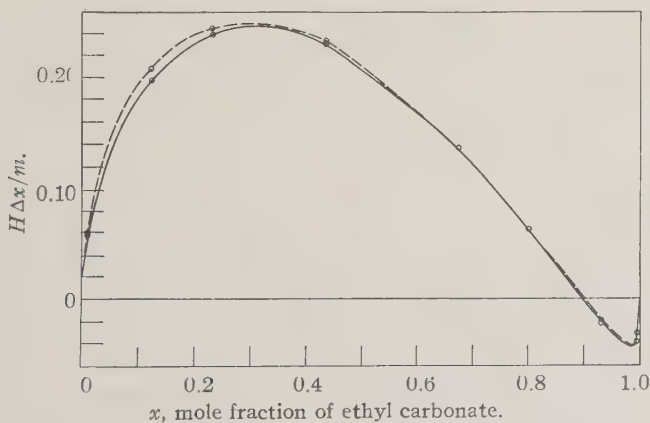


Fig. 4.—Experimental points, — — — — —; $0.8479 (x)^{0.591} (1 - x) - 0.1619 (1 - x)^{0.2462} (x)$, —————. Adsorption of ethyl carbonate from methyl benzoate.

Discussion

The interferometric method had previously been used for the determination of the extent of preferential adsorption by carbon, of the components of binary non-aqueous systems over the entire range of concentration.¹ In each case investigated an S-shaped adsorption curve was obtained.

TABLE IV
ADSORPTION OF ETHYL CARBONATE FROM METHYL BENZOATE

c_0	m	c	$\frac{N(c_0 - c)}{m}$	x	$\frac{H \Delta x}{m}$
0.0106	0.2450	0.01017	0.00717	0.01172	0.06071
.1111	.2724	.10942	.02494	.12417	.20807
.2032	.2424	.20129	.03229	.23336	.27521
.4042	.2010	.40249	.03337	.43723	.26651
.6425	.3141	.64065	.02381	.67295	.13683
.7727	.2618	.77216	.00844	.79629	.06399
.9220	.2657	.92203	— .00042	.93169	— .00313
.9914	.2843	.99180	— .00520	.99516	— .03838
.9951	.2715	.99539	— .00406	.99701	— .03000

It was noted that the component having the higher adhesion tension against the carbon was preferentially adsorbed over the greater portion of the concentration range.

In the present investigation the same method was employed for the measurement of concentration changes during adsorption, but in this work silica was used as the adsorbent. It was found, as in the earlier investigation, that the component having the higher adhesion tension against the solid was preferentially adsorbed over the greater portion of the concentration range.

In general, it may be stated that the order of increasing adhesion tension values of a series of liquids against carbon is the reverse of the order of increasing values against silica. It must accordingly follow that the order of decreasing interfacial tension values of a series of liquids against carbon is the reverse of the decreasing interfacial tension values of this series of liquids against silica. One would be justified in expecting that the adsorption effects obtained with carbon would be different, in fact, practically the reverse, of the effects obtained with silica. Our results indicate that if one obtains adsorption values for a binary liquid system over the concentration range for carbon, one can by means of the adsorption curve predict with a fair degree of accuracy the degree of preferential adsorption to be expected at the different concentrations, when silica is used as adsorbent. Each adsorbent will tend to give an S-shaped adsorption curve. The one curve will tend to be the inverted and reverse form of the other. In Fig. 2 are plotted curves showing preferential adsorption values for benzene and for ethyl alcohol adsorbed with carbon and with silica. When carbon was used as the adsorbent, the non-polar liquid benzene was much more highly adsorbed than was the polar liquid alcohol; also, benzene was preferentially adsorbed over the greater portion of the concentration range.¹ With silica as adsorbent, the alcohol was more highly adsorbed than was benzene and it was also preferentially adsorbed over a greater portion of the concentration range.

Zero preferential adsorption with carbon comes at a concentration of approximately 0.2 mole fraction of alcohol, and with silica at a concentration of approximately 0.82 mole fraction of alcohol. At zero preferential adsorption both components are adsorbed, but they are adsorbed in the same proportions as represented by the concentration of the bulk of the solution.

Summary

1. In a study of the adsorption by silica from non-aqueous binary systems over the entire concentration range the interferometric method was used to measure changes in concentration of solutions.

2. In each system investigated an S-shaped adsorption curve was obtained. Over some portion of the concentration range each of the components was preferentially adsorbed.

3. The adsorption curve obtained with silica as adsorbent is very nearly the inverted and reverse form of that obtained with carbon for the same binary liquid system.

4. That component having the higher adhesion tension against the solid is preferentially adsorbed over the greater portion of the concentration range.

5. The Freundlich equation when so modified as to express the measure of adsorption in terms of change in concentration, as

$$H \Delta x / m = ax^n (1 - x) - b (1 - x)^d x$$

was found to express the adsorption as determined over the entire range of concentration.

II—ADSORPTION BY SILICA AND CARBON FROM BINARY ORGANIC LIQUID MIXTURES OVER THE ENTIRE CONCENTRATION RANGE

Several different investigators have used different adsorbates, constituting an homologous series, in their studies of adsorption with silica.¹ A variety of solvents have been used in such work, but measurements have been carried out only over a limited range of concentration. The adsorbate components have usually been the fatty acids, since for these the change in concentration due to adsorption can be determined by ordinary analytical methods.

In general the results have shown that, in the different homologous series studied, adsorption from an organic solvent is positive. This is to be expected as it is known that, other factors being equal, the greater adsorption is obtained of that component which has the higher adhesion tension against the adsorbent. The adhesion tension values of the fatty acids against silica are greater than are those of the solvents used. The fatty acids, accordingly, should be preferentially adsorbed. It has been found that for the fatty acid series the adsorption is decreased as the molecular weight of the fatty acid adsorbate is increased. Since the adhesion tension values of the different fatty acids against silica are similar, the difference in degrees of adsorption is probably due to the increasing solubility tendency of the adsorbate as its hydrocarbon chain is increased.

Because of the similarity in chemical constitution of the saturated monobasic alcohols and the fatty acids it seems reasonable to expect that the order of adsorption of an homologous series of the saturated monobasic alcohols by silica from benzene should be similar to that obtained for the fatty acids from benzene. The solubility tendencies of the alcohols in benzene should increase as their molecular weights increase. This tendency then should result in a lower adsorption of the higher alcohols from benzene.

If carbon be employed as the adsorbent for the alcohol systems instead of silica, the amount of adsorption of the alcohols should be much less, for the adhesion tension values of the alcohols against carbon are lower

¹ Bartell and Fu, *J. Phys. Chem.*, **33**, 680 (1929); Holmes and McKelvey, *ibid.*, **32**, 1522 (1928); Th. Sabolitschka, *Pharm. Z.*, **74**, 382 (1929).

than the adhesion tension values against silica and, also, the adhesion tension values of the alcohols against carbon are lower than the adhesion tension of benzene against carbon. In fact, it should be expected that the preferential adsorption tendency with carbon, when considered for different concentrations extending over the entire concentration range, would be just about opposite to that with silica.

Neither volumetric nor gravimetric methods are suitable for measuring the changes in concentration of alcohols due to adsorption. Such changes were therefore measured by interferometric analysis. This method was found to be satisfactory for the determination of the slight concentration changes involved in the adsorption from the systems studied.² The accuracy of the method is high for the entire range of concentration.

Preparation of Materials.—The silica was prepared as described in a

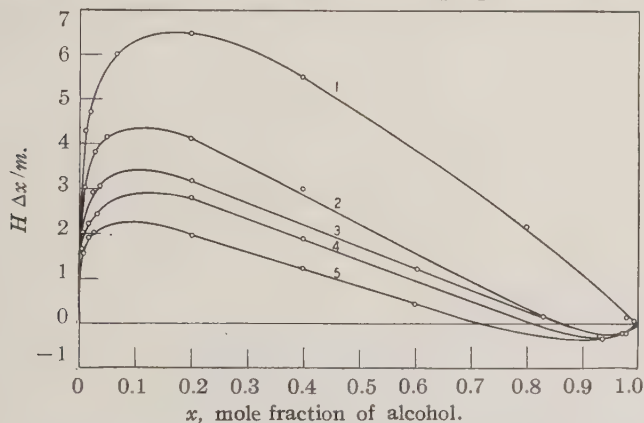


Fig. 1.—Adsorption by silica, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, *n*-propyl alcohol; 4, *n*-butyl alcohol; 5, isoamyl alcohol.

previous paper.³ A large quantity was prepared in order that all the samples used should have identical properties.

The carbon was a purified ash-free blood charcoal.⁴ It was activated by heating for twenty minutes in a muffle furnace at a temperature of 1000°. It was cooled in dry air and was transferred directly to the adsorption flasks.

Standard methods were employed in the purification of the liquids. The middle fractions only were used in this work.

Results

The results obtained are indicated in the curves presented herewith. In order to conserve space, tables of data are not given. In Fig. 1 are

² Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1637 (1929).

³ Bartell, Scheffler and Sloan, *ibid.*, **53**, 2501 (1931).

⁴ This charcoal was furnished by E. J. Miller of the Michigan Agricultural Experiment Station.

given curves for the different alcohol-benzene systems with silica. In Fig. 2 are given the curves for the different alcohol-benzene systems with carbon. The modified Freundlich equation $H\Delta x/m = ax^n(1-x) - b(1-x)^d x$ was found to apply to all of these systems. The equations applicable to each system are:

Methyl alcohol-benzene-silica

$$H\Delta x/m = 11.429 (x)^{0.215} (1-x)$$

Ethyl alcohol-benzene-silica

$$H\Delta x/m = 8.840 (x)^{0.227} (1-x) - 4.664 (1-x)^{0.615} (x)$$

n-Propyl alcohol-benzene-silica

$$H\Delta x/m = 6.807 (x)^{0.222} (1-x) - 3.733 (1-x)^{0.684} (x)$$

n-Butyl alcohol-benzene-silica

$$H\Delta x/m = 7.261 (x)^{0.222} (1-x) - 4.808 (1-x)^{0.643} (x)$$

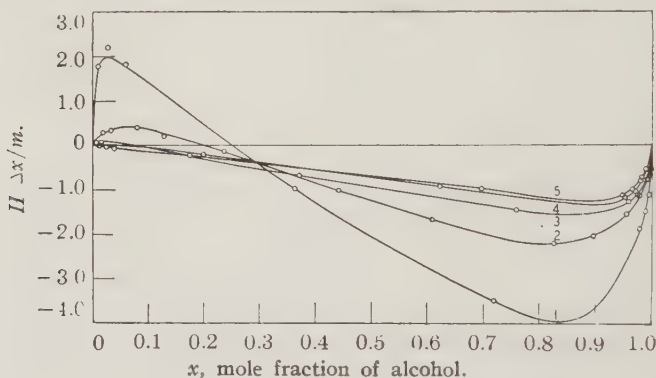


Fig. 2.—Adsorption by carbon, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, *n*-propyl alcohol; 4, *n*-butyl alcohol; 5, isoamyl alcohol.

Isoamyl alcohol-benzene-silica

$$H\Delta x/m = 4.529 (x)^{0.216} (1-x) - 3.491 (1-x)^{0.600} (x)$$

Methyl alcohol-benzene-carbon

$$H\Delta x/m = 5.327 (x)^{0.222} (1-x) - 12.218 (1-x)^{0.465} (x)$$

n-Propyl alcohol-benzene-carbon

$$H\Delta x/m = 1.496 (x)^{0.616} (1-x) - 3.819 (1-x)^{0.323} (x)$$

n-Butyl alcohol-benzene-carbon

$$H\Delta x/m = 1.738 (x)^{0.704} (1-x) - 3.475 (1-x)^{0.324} (x)$$

Isoamyl alcohol-benzene-carbon

$$H\Delta x/m = 2.716 (1-x)^{0.270} (x)$$

As indicated in Fig. 1, the preferential adsorption of the alcohols by silica from an organic solvent (benzene) having a lower adhesion tension against silica than have the alcohols, decreases as the molecular weight of the alcohols increases. Figure 2 indicates that the preferential adsorp-

tion of the series of alcohols from the same solvent by carbon is in the same order, although much less, than with silica. This is because the solvent has a higher adhesion tension against the carbon than have the alcohols. This same solvent has a relatively low adhesion tension against silica and accordingly adsorption by this adsorbent must be high.

The results obtained are consistent and are in general what were to be expected from the energy relationships of the different systems.

Two sets of results only are not as might have been predicted. The results are those obtained with the methyl alcohol-benzene system with silica and the isoamyl alcohol-benzene system with carbon. All other binary organic liquid systems which have been studied have given S-shaped adsorption curves; that is, preferential adsorption of each of the components occurred over some portion of the concentration range. With the methyl alcohol-benzene-silica system no preferential adsorption of benzene could be detected with silica as adsorbent and with the isoamyl alcohol-benzene-carbon system no preferential adsorption of isoamyl alcohol was detected. These systems were checked repeatedly since at least a slight preferential adsorption was expected over the range indicated. Special precautions were taken to insure that perfectly dry (water-free) alcohol was used, but in no case were we able to obtain evidence of negative preferential adsorption over the range indicated.

After the completion of this work and after the paper had been written (June, 1930), a paper by Jones and Outridge⁵ appeared on "Adsorption by Silicic Acid Gel in the System *n*-Butyl Alcohol-Benzene." Adsorption of the liquid components was studied over the entire concentration range. From their results they conclude, "No region occurs, in the high equilibrium concentrations of alcohol, where there is a negative selective adsorption of the alcohol" The solutions were analyzed by the "critical solution temperature" method of Jones.⁶ Their adsorption curve for the *n*-butyl alcohol-benzene system was not S-shaped. This does not agree with the results presented in this paper for this system. While we shall not at this time attempt to account for the difference in the results obtained in these two researches we have no reasons to believe that our own results covering this system are in appreciable error.

Summary

1. The monobasic alcohols of the saturated hydrocarbon series are preferentially adsorbed by silica from benzene over the greater portion of the concentration range and in an order decreasing as the molecular weight increases. The preferential adsorption by carbon from similar systems is in

⁵ Jones and Outridge, *J. Chem. Soc.*, 1513 (1930).

⁶ Jones, *ibid.*, 123, 1392 (1923).

the same order, is of much less magnitude, and occurs over but a limited portion of the concentration range.

2. The modified Freundlich equation which has been used in other investigations recently reported from this Laboratory was found to apply to the preferential adsorption effects for both the silica and the carbon adsorbents.

3. The degree of adsorption of one component, the adsorbate, from a binary organic liquid system is dependent upon the adhesion tension of that component against the adsorbent as compared to the adhesion tension of the solvent against the adsorbent, and also upon the solubility of the adsorbate in the solvent. The effect of solubility is noted when a series of compounds of similar adhesion tensions against an adsorbent are adsorbed from a given solvent, such as benzene. The greater the solubility of the adsorbate, the less will be its tendency to be adsorbed.

